IPST Technical Paper Series Number 512

Photolysis of Chlorinated Organic Compounds in Bleach Plant Effluents Exposed to Sunlight

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February 1994

Submitted to
1994 TAPPI Environmental Conference
April 17–20, 1994
Portland, Oregon

PHOTOLYSIS OF CHLORINATED ORGANIC COMPOUNDS IN BLEACH PLANT EFFLUENTS EXPOSED TO SUNLIGHT

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ABSTRACT

Upon exposure to sunlight, chlorinated organic compounds lose chlorine and undergo other structural transformations which can affect their environmental impact and fate. The purpose of this study was to obtain information about the rates and mechanisms of photolysis of the chlorinated organic constituents of wastewaters from bleached kraft mills. The rates of photodechlorination of adsorbable organic chlorine (AOX) in whole bleach plant filtrates, treated whole effluents, and high molecular weight (HMW) compounds in bleach plant filtrates were determined. The rates of photolysis, the reaction quantum yields, and photolytic reaction products of chlorinated aromatic and aliphatic model compounds were determined.

Bleach plant filtrates lose up to half of their organochlorine and one fifth of their organic carbon upon exposure to natural sunlight over a period of 8 weeks. Treated effluents become photodechlorinated as well which suggests that chemical and biological mechanisms of chlorine removal are complementary modes of AOX destruction. The HMW fraction of bleach plant filtrates loses chlorine and organic carbon directly; however, there is also probably some fragmentation to LMW material which, in turn, becomes photolyzed. Dechlorination of aromatic and aliphatic compounds in water involves the replacement of chlorine by a hydroxyl group or a hydrogen. Organic carbon can be lost through decarboxylation or decarbonylation.

INTRODUCTION

The fate of chlorinated organic compounds in wastewater treatment plants and in natural aquatic environments is an important issue to the pulp and paper mill industry. One potential pathway for the reduction of organochlorine is by photolysis. Photolytic reactions can remove the chlorine from the organic matrix and transform it to innocuous chloride ion. In addition to dechlorination, photolytic reactions can occur in which the chemical structure of the chlorine-bearing organic compounds can be altered without the removal of the chlorine. A clearer understanding of the rates, mechanisms, and potential importance of photolytic pathways may be useful for the prediction of the environmental impact of organochlorine produced from the manufacture of bleached pulp. Furthermore, information about photodechlorination could be useful in the development of photolytic treatment technologies and for the optimization of wastewater treatment plants.

In these studies we determined the rates of photodechlorination of adsorbable organic chlorine (AOX) in bleach plant filtrates and treated whole effluents. We also investigated photodechlorination of high molecular weight (> 1,000 daltons) AOX in bleach plant filtrates; total AOX reduction, the influence of pH and oxygen, and the production of low molecular weight (< 500 daltons) chlorinated organic compounds were evaluated. We determined the rates of photolysis, the reaction quantum yields, and photolytic reaction products of model compounds that are representative of effluent constituents (mucochloric acid and 3,5-dichloro-4-hydroxybenzoic acid).

EXPERIMENTAL

Photolysis of Whole Wastewaters

The rates of dechlorination were determined for whole bleach plant filtrates and treated whole effluents obtained from an integrated kraft mill using softwood and hardwood furnish. The filtrates were obtained by sampling at the filtrate pumps in a 4:10:4:10:4 volume ratio from the bleach plant using a C_{90}/D_{10}EoDEoD sequence. The treated effluents were obtained at the point of river discharge after a primary clarifier and an aerated lagoon with a 6-day hydraulic retention time. Both wastewaters were stored at 4°C until used. Both samples were filtered through a 0.45 um filter; 0.1% sodium azide was used as a biocide. Preliminary experiments showed that the azide did not affect the rate of photolysis at the pH used in these studies (7-8).

The wastewater samples (27 mL) were placed in 1.7 x 15 cm borosilicate tubes with 1 mm walls. Preliminary experiments showed that there was not a significant difference in the extent of AOX degradation between samples in similarly sized quartz tubes and in the borosilicate tubes after 17 hours of sunlight exposure. Controls consisted of tubes wrapped in aluminum foil.

The tubes were attached to a black board which was placed in direct sunlight for several hours per day when there was little cloud cover. Between exposures, the samples were covered in black plastic and stored at 4°C. The experiments took place in

Atlanta, GA, July-August 1993. The sum of solar irradiance at wavelengths 297.5 to 800 nm has been estimated to be 22.3 millieinsteins $cm^{-2}day^{-1}$ at 30°N latitude in the summer on clear days (1,2). These values were used in calculations for environmental rate constants and reaction quantum yields. Duplicate samples were withdrawn and analyzed at regular intervals of sunlight exposure.

Several samples were aerated two times throughout the experiment by gently bubbling air through the solutions; there was no significant difference in the extent of dechlorination between the tubes that had been aerated and those that had not. Temperatures varied from 27 to 40°C.

The pseudo first-order rate constants were calculated from the slope of a linear regression of ln Co/Ct vs. hours exposed using the method of least squares. Half-lives were calculated from 0.693/k.

Photolysis of High Molecular Weight AOX

Filtrates from C/D stage and Eo stages were collected from a softwood kraft bleach plant using a sequence of C_{70}/D_{30} EoDED. The filtrates were combined in a 60:40 volume ratio, adjusted with sulfuric acid to pH 7, frozen and shipped to Niro Hudson, Inc. for ultrafiltration. The sample was ultrafiltered at 6 bar and 30°C using a GR-90 polysulfone filter. The filtrate was concentrated to one eighth of its original volume and then flushed with 3 volumes of water. Although this procedure theoretically removes 99.5% of the low molecular weight species, we found approximately 20% of the AOX and TOC had a molecular weight below 500 daltons using a second ultrafiltration at constant, diluted volume, probably due to aggregation of low molecular weight materials at high concentrations. Charge exclusion of ionized species at neutral pH may also contribute to low molecular weight material in an apparently high molecular weight fraction. In this study, we do not address the issue of aggregation and association of LMW compounds with HMW compounds (3); therefore, HMW and LMW are operationally defined to mean those fractions that are retained and are not retained by ultrafiltration membranes, respectively. After filtration through a 1.5-micron glass fiber filter, the sample was diluted to its original concentration using phosphate buffers (ionic strength = 3) to maintain pH at 5, 7, and 8. Sodium azide was added at a concentration of 0.1%.

The filtrates were placed in 500 mL borosilicate bottles. Dark controls consisted of bottles wrapped in black tape with an outer layer of masking tape. Some of the samples were aerated by gently bubbling air through the solutions for 20 minutes two times a day. Anoxic conditions were maintained by purging the samples with nitrogen for 10 minutes and carefully sealing. The samples were maintained in a greenhouse in Atlanta, GA, from October to November 1992. The temperature was maintained between 20 and 40°C.

The influence of pH, oxygen, and light was evaluated in a 2^3 factorial design experiment. High conditions were light, pH = 8 and oxygen, while low conditions consisted of dark, pH=5 and anoxic conditions. After 12 weeks, the samples were analyzed for AOX and TOC. In a time series experiment, duplicate samples (oxygenated, pH = 7, exposed to light) were withdrawn every 2 weeks for 8 weeks and analyzed for whole AOX and TOC. Portions of these samples were fractionated into high molecular weight (>500 daltons) and low molecular weight portions using diafiltration. The diafiltration was conducted using an Amicon YC-05 filter; the sample volume, which was constant throughout the process, was replaced 5 times.

Photolysis of Model Compounds

The model compounds consisted of an unsaturated aliphatic chlorinated compound with carbonyl and carboxylic acid functional groups (mucochloric acid (MA)) and a chlorinated aromatic acid (3,5-dichloro, 4-hydroxybenzoic acid (BA)). The initial concentrations of the samples were [MA] = 1 mM and [BA] = 2 mM. Mixtures of the compounds were dissolved in 5% acetonitrile, rather than the recommended 1% acetonitrile (1,2), due to solubility limitations. Half of the samples were dissolved in a diluted oxygen stage filtrate containing approximately 100 mg/L total organic carbon in addition to the acetonitrile.

An actinometer composed of p-nitroacetophenone and pyridine was photolyzed under the same conditions as the samples in order to estimate the reaction quantum yield of the model compounds. The half-life of the p-nitroacetophenone was intermediate to the half-lives of the two model compounds. Procedures were carried out in accordance to the methods outlined in EPA method CG 6000 (1), except as otherwise noted.

Mixtures of both compounds were photolyzed in the same manner as the whole bleach plant filtrates and effluents described above. The reaction quantum yields of the compounds (ϕ) were calculated from

$$\phi^c_E = \frac{k_p^c \, \Sigma \varepsilon_\lambda^a \times L_\lambda}{kp^a \, \Sigma \varepsilon_\lambda^c \times L_\lambda} \; \phi^a_E$$

where ε = molar absorptivity; L = solar irradiance; the a superscripts refer to the actinometer; the c superscripts refer to the model compounds; and the E subscript refers to environmental values. $\phi^a_E = 1.4 \times 10^{-4}$ when pyridine is 1.1×10^{-5} M and $\Sigma \varepsilon_\lambda^a \times L_\lambda = 551$ $days^{-1}$ at 30°N latitude in the summer. The environmental rate constants were calculated by $kpE = \phi^c_E \, \Sigma \varepsilon_\lambda^c \times L_\lambda$ (1,2). These values should be considered estimates because of the use of borosilicate tubes.

Analyses

The AOX was measured by the batch method (SCAN-W 9:89) using a Dohrman Model DX-20 TOX Analyzer. The TOC was measured by acidifying to pH < 2 with sulfuric acid, purging with nitrogen, and analyzing with a Beckman Model 915-B TOC Analyzer. The molar absorptivities were calculated from absorbances obtained from a Perkin Elmer Lambda 4-B spectrophotometer with a 1.0 cm pathlength. Chloride concentrations were obtained from an Orion electrode.

The concentrations of model compounds and the actinometer were analyzed using a HP 1090 liquid chromatograph equipped with a photodiode array detector and a 100 x 4.6 mm C-18 column. The mobile phase was 72% acetic acid solution (2%) and 28% acetonitrile with a flow rate of 1.5 mL/min. External standardization was used to quantify all compounds; the wavelength used for quantitation for p-nitroacetophenone and BA was 260 nm and 250 nm for MA.

Reaction products were evaluated by extraction of the samples with diethyl ether, methylation of the concentrated extracts with diazomethane (4), and analysis by gas chromatography/mass spectrometry using a HP 5890 GC equipped with a HP 5917A-MSD in EI mode. GC conditions were as follows: injector - 280°C, oven - initial 50°C, 1 minute hold, 8°C/min. to 295°C. Identifications were made on the basis of library matches (NBS); tentative identifications were made on the basis of molecular weights and fragmentation analyses.

RESULTS AND DISCUSSION

Photolysis of Whole of Wastewaters

The reduction of AOX in whole wastewaters with time of exposure to sunlight is shown in Figure 1. The initial AOX concentration in the bleach plant filtrates was 52 mg/L and 13 mg/L in the treated effluent. After 44 hours of exposure to sunlight, 33% of the AOX in the bleach plant filtrates was dechlorinated, while 42% of the AOX in the treated effluents was removed. Although there was a slight leveling off of the rate of dechlorination, the removal of chlorine was clearly still occurring at the end of the experiment after 44 hours of irradiation. Chloride concentrations in the sample from the final time period accounted for all of the loss of AOX confirming that complete mineralization of the AOX took place.

The rate constants for the overall dechlorination of the two wastewaters, shown in Table I, were not significantly different at the 95% confidence level. Furthermore, the data showed that more nonphotolytic dechlorination occurred in the treated effluent than in the bleach plant filtrates (14% for the treated effluent at 44 hours exposure compared to 7% reduction in bleach plant filtrates). When rate constants were calculated for photodechlorination only, the difference in the constants between the two wastewaters decreased, and the photolytic half-lives were 1-2 days longer than the overall half-lives. It is interesting to note that in preliminary experiments in which diluted treated effluent was examined, there was significantly more degradation of the AOX (52%) (data not shown), probably because of less light attenuation in the lighter colored samples.

The similarity in the rates of dechlorination of the treated effluents and the bleach plant filtrates was informative. The fraction of AOX that is easily degraded biologically must be different from the fraction of AOX that can be dechlorinated photolytically. Given the susceptibility of the treated effluent to both nonphotolytic and photolytic dechlorination, it is reasonable to suppose that both chemical and biological dechlorination are important mechanisms of AOX removal and that these pathways may operate synergistically.

The rates of dechlorination of the two whole wastewater samples were comparable to values obtained in laboratory photolyses of high molecular weight AOX in bleach plant filtrates performed by other researchers (5). The similarity in the photolytic behavior of high molecular weight AOX and whole AOX suggests that low and high molecular weight AOX are equally susceptible to loss of chlorine by photolytic mechanisms. The importance of this behavior is discussed more fully below.

There was a substantial change in the UV-visible absorbance of the wastewaters with time. Significant decreases in absorbance between 250-260 nm occurred. It is unknown whether these changes were induced by light or by nonphotolytic mechanisms. In addition, unbuffered samples exhibited a steady decrease in pH with exposure, indicating the formation of carboxylic acids.

Photolysis of HMW AOX

Results from the factorial design experiment showing the effect of pH, oxygen, and light on HMW AOX are given in Figure 2. Maximum AOX reduction occurred under conditions of light and oxygen. All three variable were important in dehalogenation after 12 weeks exposure. Light was by far the most significant variable, confirming that photodechlorination was a major mechanism of AOX loss.

Lower pH enhanced dehalogenation when light was present under anoxic conditions, but higher pH promoted nonphotolytic dehalogenation. This finding is consistent with studies which show that more oxidative dechlorination takes place at higher pH (6). However, the pH range examined in this study was small, and the pH effect was small as well.

It was significant that there was no interaction between the variables of light and oxygen; i.e., the photodechlorination was not dependent on the presence of oxygen. The absence of effect of oxygen on photodechlorination rates and reaction products has also been observed in studies examining mechanisms of aromatic dechlorination (7,8). While photodechlorination did not depend on oxygen, the presence of oxygen by itself caused some dechlorination. The high level of aeration in this experiment may have promoted purely oxidative dechlorination which has not been observed in similar studies (9).

Anoxic, nonphotolytic dechlorination took place at the higher pH, but was insignificant at pH 5. The prominence of reductive dechlorination was also reported by Fitzsimons et al. (10) who concluded that chemical reductive dechlorination may play a significant role in the loss of chlorine from HMW chlorolignin under anaerobic conditions.

From these data it appears there are at least two nonphotolytic chemical mechanisms of dechlorination of HMW AOX; however, their contribution is small compared to the large contribution of photolysis to dechlorination of HMW AOX.

Maximum loss of total organic carbon (27%) occurred in conditions of light, low pH, and oxygen (Figure 3). Lower pH promoted photolytic removal of carbon. There was little effect of oxygen on the reduction of organic carbon at low pH, while oxygen promoted TOC reduction at higher pHs. These data suggest that there are separate photolytic and oxidative mechanisms of TOC removal under mild conditions of pH, light, oxygen, and temperature.

In the time series experiment, AOX and TOC were monitored over 8 weeks under conditions of light, aeration, and at pH = 7 (Figure 4). The initial HMW AOX concentration was 16 mg Cl/L. After an initial lag, total AOX decreased rapidly between weeks 4 and 6, ultimately reaching a 56% reduction. Although a lag phase has been noted by other researchers investigating laboratory photodechlorination of E1 stage AOX (11), in this study, the lag phase corresponds to cloudy weather conditions. Thus, it is probable that these data do not reflect a mechanism which incurs a chemical lag phase.

Chloride concentrations in the sample from the final time period accounted for all of the AOX reduction, which confirmed that complete mineralization of the AOX took place.

The majority of the AOX reduction occurred by the 6th week of exposure at which point a leveling off of the AOX reduction occurred. Approximately 44% of the HMW AOX appeared to have a much slower rate of dechlorination than the rest of the HMW AOX. This finding is similar to the recalcitrant fraction of AOX found in laboratory photolytic studies by Caron and Reeve (5) (47%). Chlorophenols in pulp bleach plant effluents also exhibited a leveling-off effect (11). Archibald and Roy-Arcand (9) found ongoing dechlorination, albeit at a slower rate, even after 16 weeks of exposure of hardwood HMW AOX to filtered light and a 60% reduction in AOX. If the curve in Figure 4 is extended to 16 weeks, a similar amount of AOX removal would be seen.

Total organic carbon, originally at a concentration of 109 mg C/L, gradually decreased until the eighth week when the rate of decrease leveled off at approximately 90 mg C/L. A possible means of carbon loss may be decarboxylation of conjugated carboxylic acids which are structures that occur in bleach plant filtrates (12,13). Carboxylic acids such as malonic acid, beta unsaturated acids, and beta keto acids will decarboxylate upon heating to produce CO_2 (14) which may account for nonphotolytic reduction of TOC that occurred in the factorial experiment (5-9% reduction in TOC). Because the factorial experiments also showed that exposure to light was significant, it is possible that additional decarboxylation reactions are induced by light. Laboratory photolyses have shown that decarboxylation of beta unsaturated acids can occur by indirect photolysis in the presence of quinones and aryl ketones (15,16). Given the diverse nature of organic material in bleach plant filtrate, it is conceivable that similar functional groups in the effluents could serve the role as sensitizers for decarboxylation reactions. However, it is important to note that carboxylic acids increase during exposure of effluents to light (17,18). Thus, if decarboxylation does take place, there must be a continued source of carboxylic acids, such as oxidative cleavage of aromatic rings.

If HMW AOX degrades into LMW AOX, the bioavailability and biological impact of the AOX could change. To determine whether LMW compounds arise from photolytic fragmentation of HMW components of bleach plant filtrates, we fractionated each sample in the time series experiment into a low molecular weight (MW < 500 daltons) and high molecular weight fraction. The TOC and AOX was measured in the high molecular weight fraction and the AOX was measured in the low molecular weight fraction as well (method detection limits prohibited direct measurement of TOC in the filtrates).

The majority of the reduction of the AOX and TOC occurred in the high molecular weight fraction (Figures 5 and 6). A one way analysis of variance indicated no significant difference (95% confidence) in the LMW AOX and TOC at different times. However, the proportion of LMW compounds increased. Visual inspection of the data suggests that additional samples and experimentation may reveal a small difference in TOC concentrations with time.

There are two mechanisms by which the concentration of HMW AOX and TOC may decrease with little or no changes in the concentration of the LMW fraction. The HMW components may lose Cl^- and carbon directly resulting in no change in the LMW fraction. Alternatively, the HMW components may fragment to LMW components which in turn lose Cl^- and carbon. If there is a steady state between the HMW reactions and the LMW reactions, no accumulation of LMW components will be observed.

Both mechanisms are likely to occur. The HMW (>500 daltons) C:Cl increased with time (Figure 7), suggesting that some direct dechlorination of the HMW occurs. Other researchers have found evidence for the formation of small amounts of LMW material with photolysis of HMW components of bleach plant filtrates (5,9). Furthermore, it is unlikely that the LMW fraction was resistant to reaction. Photodechlorination of many LMW compounds is well-documented (7,8,19,20) and has been observed in this study (below).

Photolysis of Model Compounds

Mucochloric acid and 3,5-dichloro-4-hydroxybenzoic acid (Figure 8) were selected because they contain structures that are prevalent in bleaching filtrates including aliphatic carbon, aromatic carbon, carboxyl groups, and double bonds conjugated with carbonyl groups (12,13,21). The rate information for the disappearance of the model compounds is given in Table II. It is interesting to note that the half-lives of the whole bleach plant filtrates and the treated effluents (Table I) lie between the half-lives of the two model compounds.

The aliphatic compound reacted much more quickly than the aromatic compound. At least two factors are important in rates of photolysis: the absorption of light and the reaction quantum yield (moles of compound transformed per quantum of light absorbed). The MA absorbs much less light than BA at environmentally relevant wavelengths ($\Sigma \varepsilon_\lambda \times L_\lambda = 8.43$ day^{-1} for MA, 60.18 day^{-1} for BA). However, MA is much more efficiently transformed by the light that it does absorb (ϕ = 0.012 for MA, 0.001 for BA). One photolytic pathway is the cleavage of the C-Cl bond. The ease of the aliphatic Cl removal over the aromatic Cl may be related to the lower bond energy of the C-Cl bond in the aliphatic compound (22).

The rate of photolysis is slower in the environment than in tubes (1,2). The rate constants of MA and BA are calculated to be 60% lower in the environment. These values still represent quite short environmental lifetimes. Assuming MA and BA simulate AOX in wastewaters, environmental photodechlorination would potentially serve as an important mechanism of AOX destruction in relatively short periods of time in aquatic environments.

The presence of the organic material in the solution did not significantly alter the rate constants. While light attenuation was expected to cause a reduction in rate, it was not observed. Either the light attenuation was insignificant or the occurrence of sensitized or indirect photolysis counteracted the reduction in rates of direct photolysis. If the organic material was a sensitizer, it did not cause a detectable difference in the reaction products. The HPLC chromatograms of the samples photolyzed in both water and organic solution were identical, suggesting that the pathways of compound disappearance were identical in the two systems.

Approximately 65-80% of the disappearance of the model compounds could be accounted for by the appearance of chloride. For example, if the model compounds that reacted lost both of their chlorines (i.e., if there was complete mineralization of chlorine), then the maximum possible chloride concentration for 56.5 hours of exposure would be 3.5 mM. The average measured concentration was 2.7 mM (% relative standard deviation = 17%) which represents 77% of the total possible mineralization. These results indicate that some of the chlorine remains bound to the transformed model compounds.

The identified reaction products, shown in Figure 8, are consistent with the chloride results. The mucochloric acid undergoes photohydrolysis which replaces a chlorine with a hydroxyl group, and photoreduction which replaces the chlorine with a hydrogen. The latter result is highly interesting because hydrolysis reactions are generally found to be far more prevalent than reduction in water (7,8,20). These types of reactions are generally independent of the presence of oxygen (7,8) which correlates with the results from the wastewater photolyses. Another interesting result was the loss of the carbonyl group. It is unclear if there was photodecarboxylation, which is known to occur (15,16) with subsequent oxidation of the aldehyde to an acid, or if there was direct removal of the aldehyde. The reaction products from the aromatic compound were comparable. Products were found from photohydrolysis, photoreduction, and decarboxylation. In addition, several aliphatic diacids were detected which may have arisen either from the mucochloric acid or from ring cleavage of the benzoic acid. Some of the diacids were monochlorinated.

The reactions shown to occur in model compounds are likely to occur in the bleach plant effluents. Dechlorination by photohydrolysis and photoreduction are likely to take place, and decarboxylation or decarbonylation of both aromatic and aliphatic constituents of filtrates could contribute to the observed reduction in TOC upon photolysis of bleach plant filtrates. However, the consistent drop in pH with photolysis of wastewaters (data not shown) indicates there must be a net formation of carboxylic acids. Acid formation has been reported by researchers investigating photolysis of chlorolignin (17,18). Therefore, as carboxyl groups are removed, other carboxylic acids are formed, possibly by way of ring cleavage (8).

The structural changes in the model compounds caused by photolysis suggest that AOX in aquatic environments will be reduced and also become significantly modified. A higher proportion of the AOX may become aromatic in nature. Changes in the polarity of the effluent constituents may occur as chlorine is replaced with either hydroxyl groups or hydrogen which could affect the ultimate fate of the chlorinated organic material.

CONCLUSIONS

Low and high molecular weight chlorinated organic compounds in bleach plant filtrates are significantly dechlorinated upon exposure to natural sunlight over a period of several weeks. In addition, organic carbon is also photolytically removed from the low and high molecular weight fractions. Chlorinated compounds in treated effluents are as susceptible to photodechlorination as untreated components of bleach plant filtrates which suggests that chemical and biological mechanisms of chlorine removal are complementary modes of AOX destruction. Nonphotolytic chemical degradation also contributes to AOX degradation; the extent is small compared to photolytic degradation.

The high molecular weight fraction of bleach plant filtrates loses chlorine and organic carbon directly. However, it is likely that there is some fragmentation to low molecular weight material which, in turn, becomes dechlorinated and loses organic carbon.

Dechlorination can occur by photohydrolysis and photoreduction in which chlorine is replaced by a hydroxyl group and a hydrogen, respectively. Carbon in model compounds, and possibly in effluents, is lost through decarboxylation or decarbonylation. Concurrent formation of additional acids, possibly by way of aromatic ring cleavage, must also occur.

The AOX from pulp and paper mills can be reduced and significantly modified in structure by photolytic pathways in aquatic environments. The environmental fate and impact of the AOX may be affected by these photolytic transformations.

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ACKNOWLEDGMENTS

Portions of this work were used by SJW as partial fulfillment of the requirements for the M.S. degree at the Institute of Paper Science and Technology. The authors wish to thank Mr. Todd Schwantes for his invaluable technical assistance with AOX and TOC measurements and Dr. T. J. McDonough for his help with the statistical design and interpretation of the HMW AOX studies.

TABLES

Table I. Rate constants and half-lives for the reduction of AOX in whole wastewaters.

	Bleach Plant Filtrates	Treated Effluent
All AOX Reactions		
k_p (hours^{-1})[a]	0.009 ± 0.0023	0.011 ± 0.0031
$t_{1/2}$ (hours)	77	64
Photolytic AOX Reactions		
k_p (hours^{-1})[a]	0.007 ± 0.0038	0.008 ± 0.0038
$t_{1/2}$ (hours)	100	83

[a] The 95% confidence interval is given.

Table II. Rate constants and half-lives for the photolysis of model compounds.

	MA in Water	BA in Water	MA in Filtrate	BA in Filtrate
k_p (hours^{-1})[a]	0.019 ± 0.0047	0.008 ± 0.0020	0.019 ± 0.0024	0.007 ± 0.0015
$t_{1/2}$ (hours)	37	86	36	94
ϕ	0.0124	0.008	-	-
k_{pE} (hours^{-1})	0.007	0.003	-	-
$t_{1/2\ E}$ (hours)	94	218	-	-

[a] The 95% confidence interval is given.

FIGURES

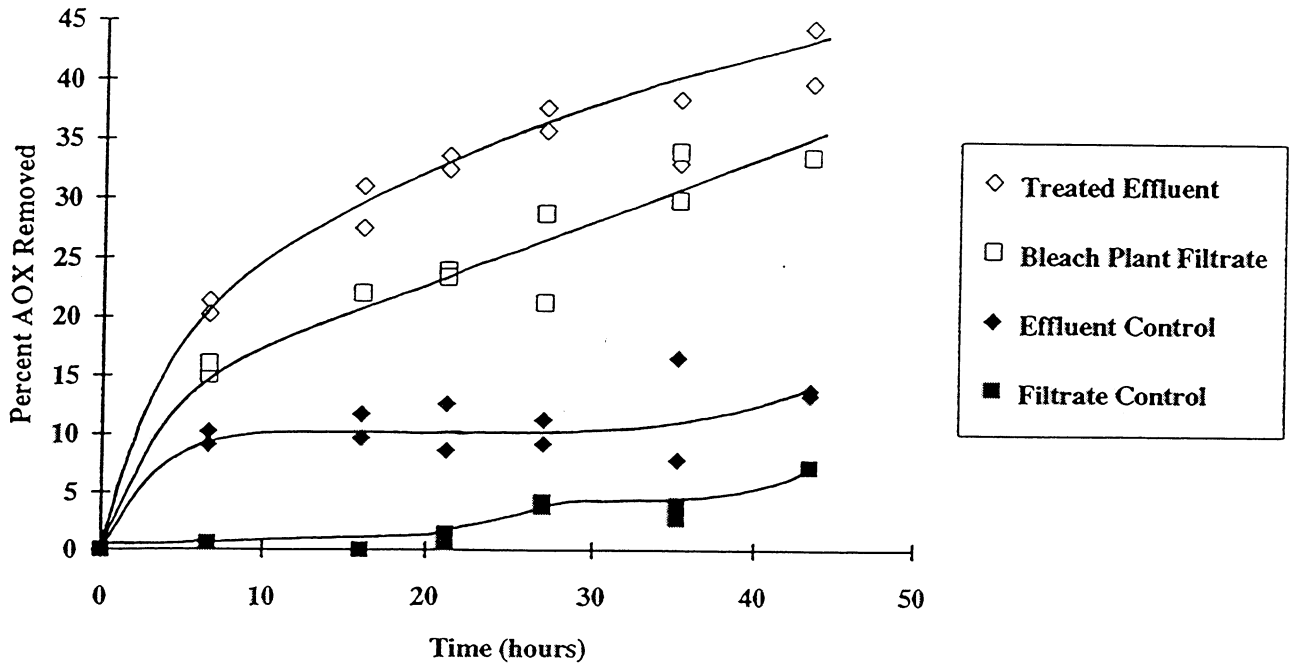

Fig. 1. Reduction of AOX in whole wastewaters with exposure to sunlight.

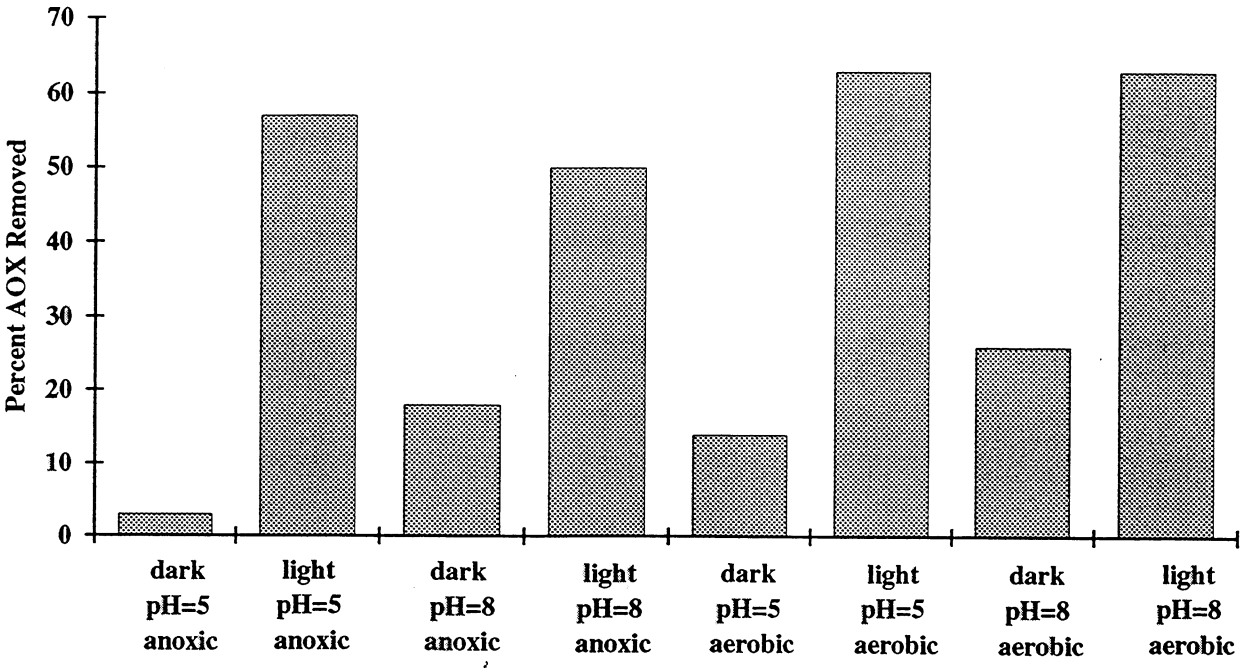

Fig. 2. Influence of light, pH, and oxygen on HMW AOX reduction.

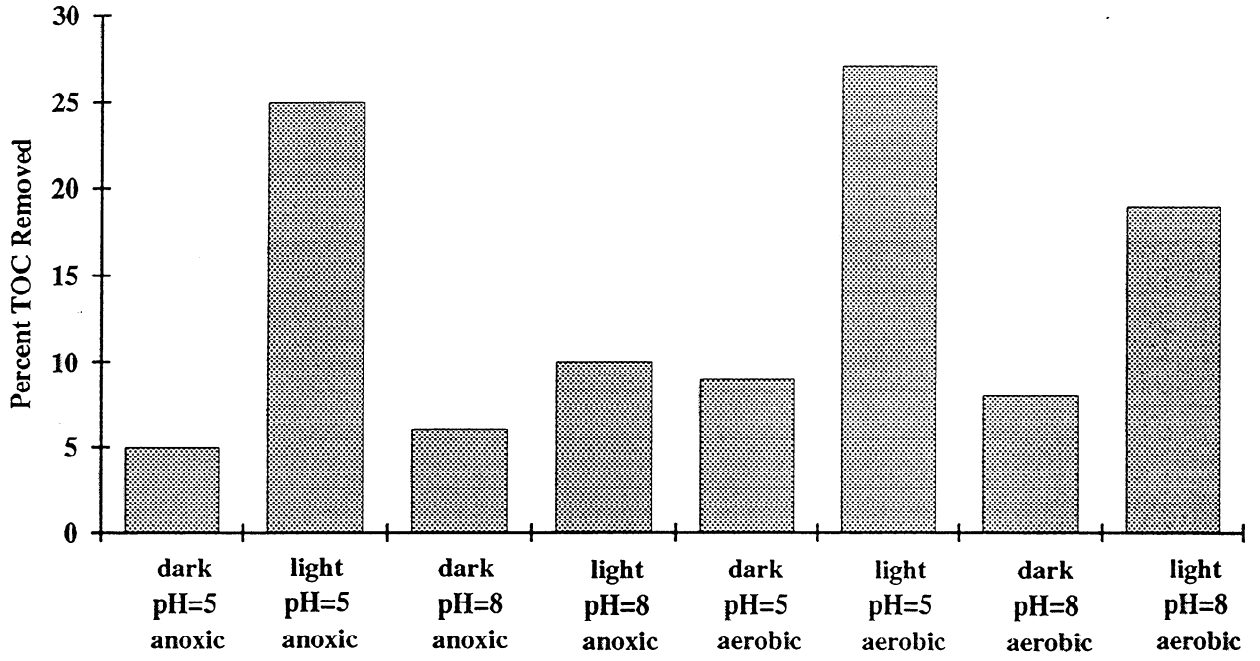

Fig. 3. Influence of light, pH, and oxygen on HMW TOC reduction.

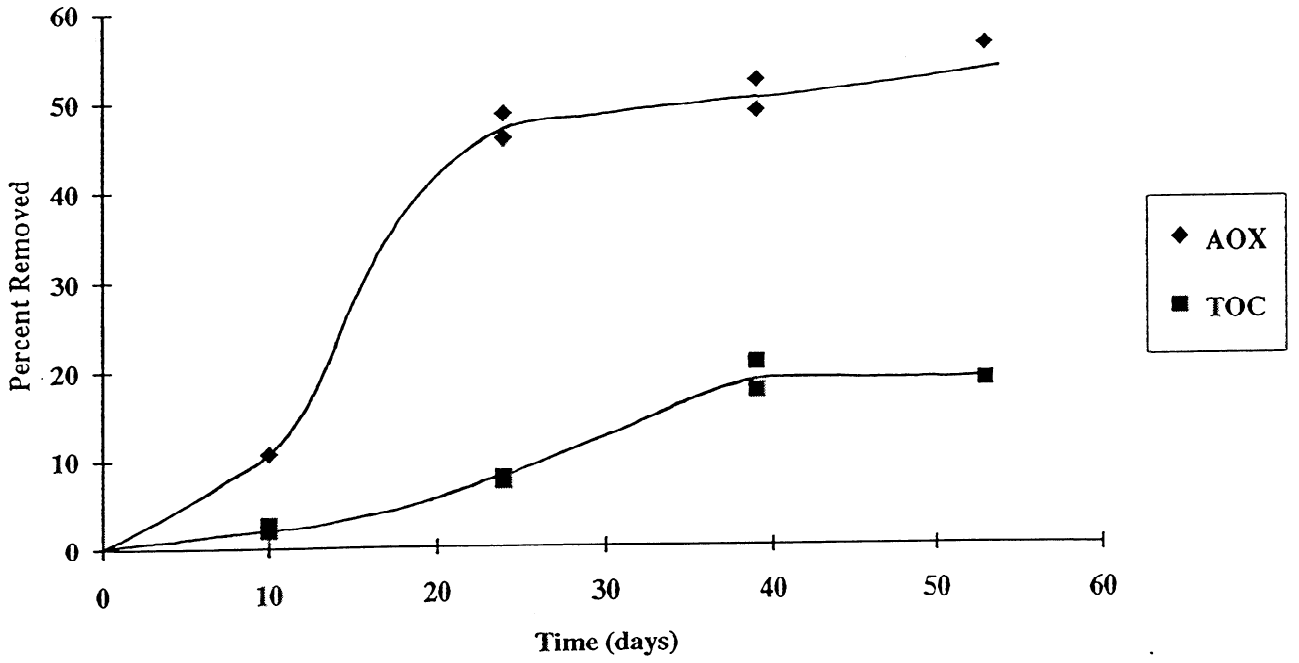

Fig. 4. Reduction of HMW AOX and TOC in bleach plant filtrates with exposure to sunlight.

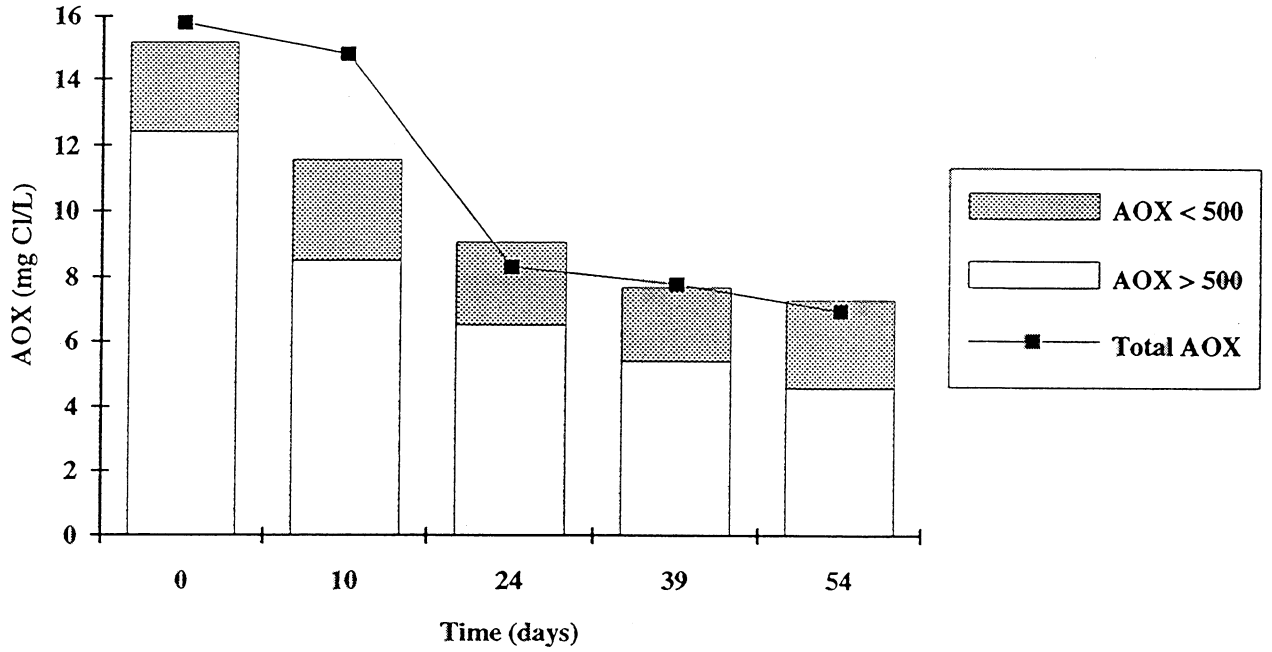

Fig. 5. Molecular weight distribution of AOX after exposure to sunlight. Total AOX is the value obtained from measurement of the whole effluent.

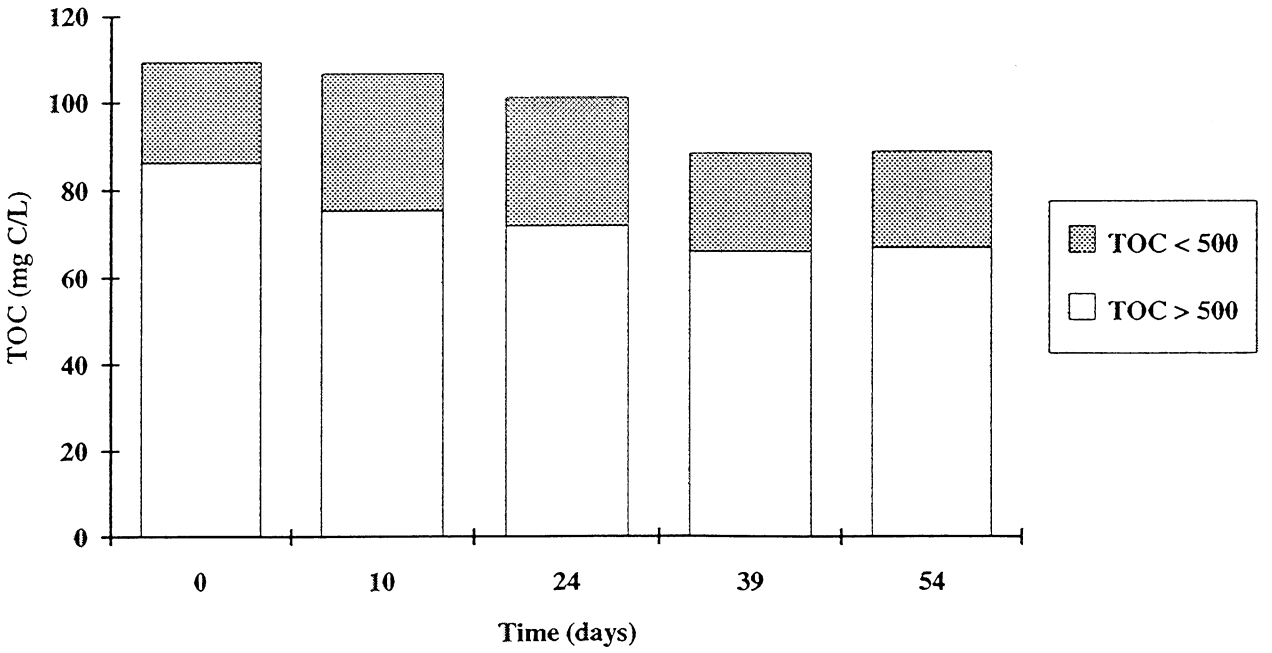

Fig. 6. Molecular weight distribution of TOC after exposure to sunlight.

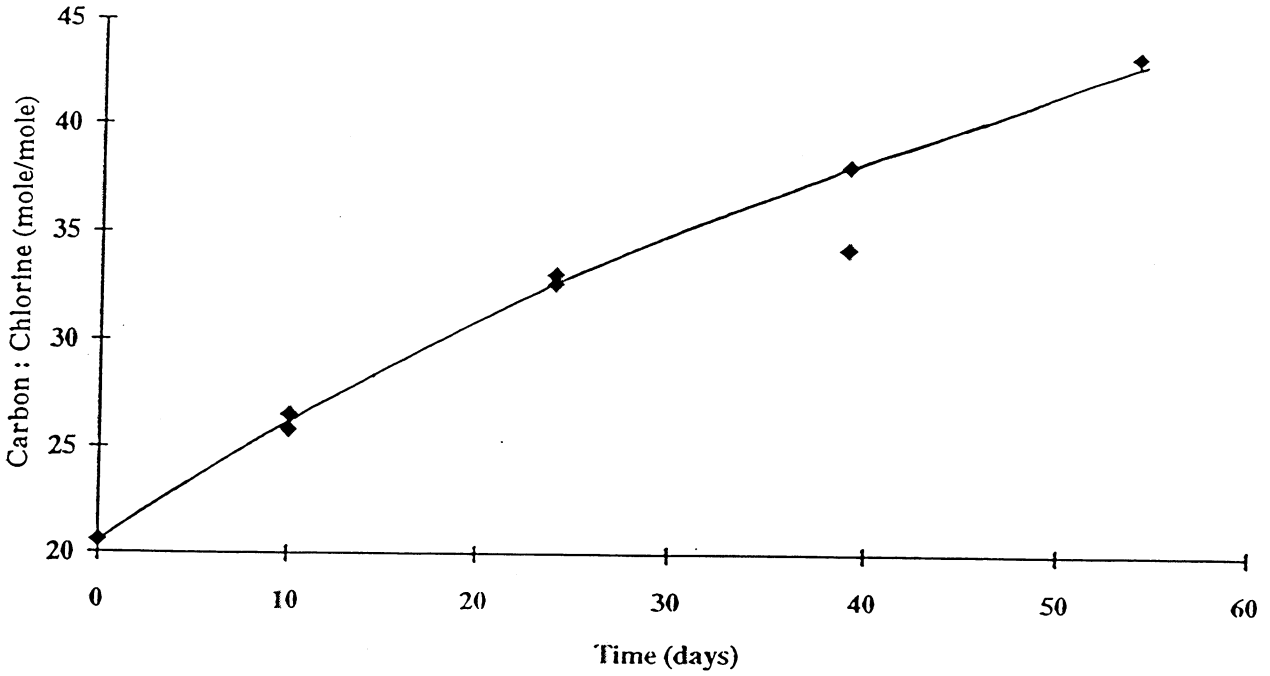

Fig. 7. Carbon to chlorine molar ratios of HMW (> 500 daltons) fractions after exposure to sunlight of HMW bleach plant filtrates.

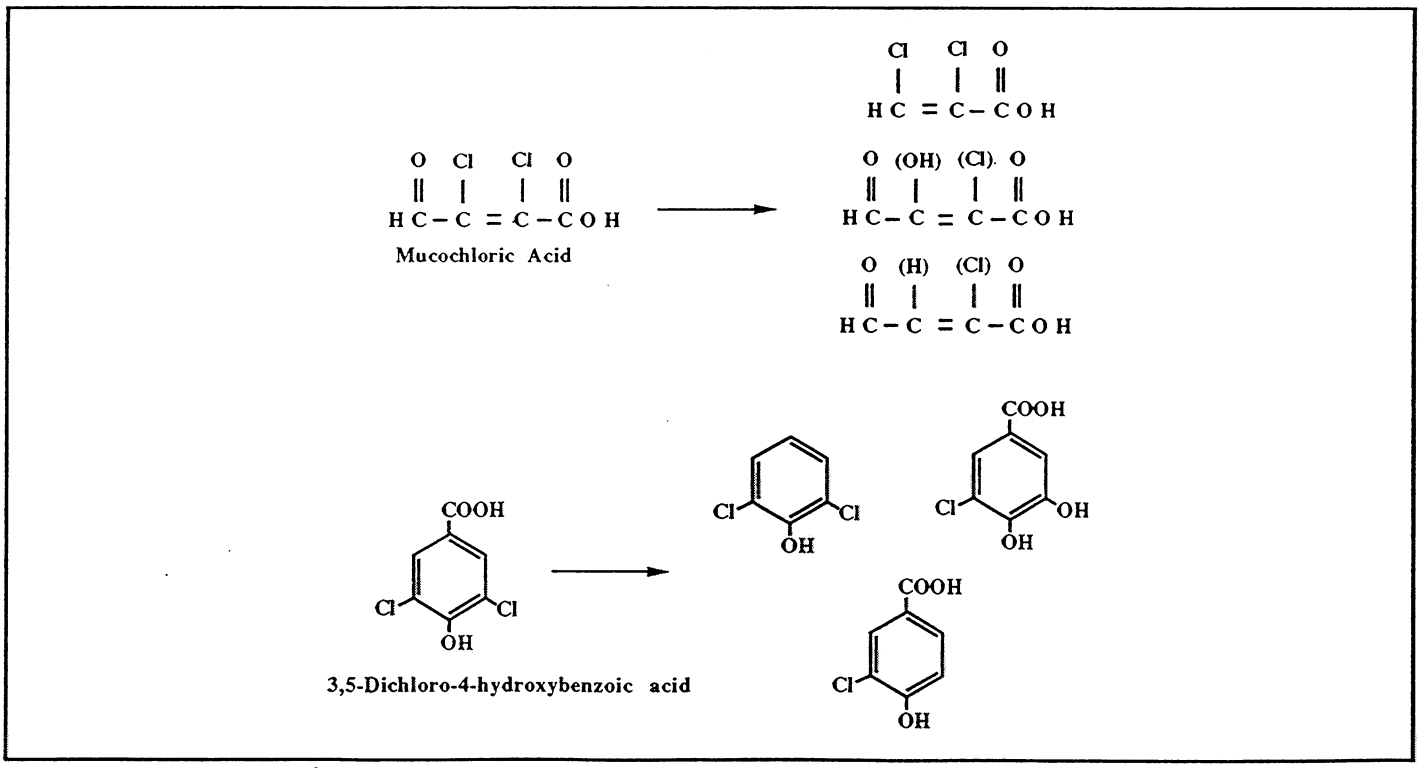

Fig. 8. Reaction products from model compounds exposed to sunlight. Groups in parentheses may be substituted on alternate carbon atoms.